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(54) Manufacturing of high molecular weight polyester.

(57) A polybutylene terephthalate is manufactured by the steps of polycondensating in the liquid phase terephthalic acid, or a lower alcohol ester thereof, as the acid component, and 1,4-butanediol as the diol component, to obtain a prepolymer of polybutylene terphthatate, solidifying the prepolymer, and further polymerizing the prepolymer in the solid phase to obtain a polybutyrene terephthalate of a higher polymerization degree, 0.001% to 5% by weight, based on the prepolymer, of a nucleator being added to the polymerization mixture, at any time during or following the monomer-mixing stage and before the start of the solid phase polymerization, the solid phase polymerization being conducted in the presence of the nucleator uniformly dispersed in the polymerization mixture.

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Manufacturing of High Molecular Weight Polyester

The present invention relates to a method of manufacturing, by solid phase polycondensation, high molecular weight polyesters mainly comprising polybutylene terephthalate, and more particularly, it provides a manufacturing method for obtaining highly polymerized polybutylene terephthalate efficiently and economically.

The State Of The Art

While polybutylene terephthalate, because of its excellent moldability and physical properties, is finding widespread use in the field of plastics for industrial applications, including automobile parts, electric appliance parts, gears, etc., its mechanical properties are highly dependent on the degree of polymerization of the starting polymer and, therefore, it is essential to manufacture a highly polymerized polymer, and to achieve this manufacture economically by whatever means, for polybutylene terephthalate to be used as a preferable starting polymer in the field of industrial plastics where excellent mechanical

properties, in particular strength, are demanded. This is a technical problem which is still open to more advantageous solutions.

Conventional methods of manufacturing highly polymerized polybutylene terephthalate include one wherein the latter half of the polycondensation reaction is carried out in a solid phase.

According to this method, generally, the polycondensation is conducted in a molten state by the conventional method; the sticky molten polymer is taken out of the polycondensator and cooled to solidity; the solidified molten polymer is ground; the ground polybutylene terephthalate (prepolymer) is dried for a substantial period of time to crystallize, and held at a temperature lower than its melting point by 5° to 60°C, to carry out solid phase condensation, thereby manufacturing polyester. In this final manufacturing stage, in the solid phase, an increase in the molecular weight occurs and especially high molecular weights may be attained under appropriate reaction conditions.

In the conventional solid phase polymerization process, drying and crystallization are of essential importance as pretreatments and, therefore, a long time is required for performing the solid phase polymerization, resulting in low productivity and high polymer cost.

The object of the invention is to attain a high degree of polymerization by the solid phase polymerization of polyester mainly comprising polybutylene terephthalate; and thereby achieve high production efficiency coupled with low cost.

Summary of the Invention.

According to the invention, a polybutylene terephthalate is manufactured by the steps of polycondensating in the liquid phase terephthalic acid, or a lower alcohol ester thereof, as the acid component, and 1,4-butanediol as the diol component, to obtain a prepolymer of polybutylene terephthalate, solidifying the prepolymer, and further polymerizing the prepolymer in the solid phase to obtain a polybutyrene terephthalate of a higher polymerization degree, 0.001% to 5% by weight, based on the prepolymer, of a nucleator being added to the polymerization mixture, at any time during or following the monomer-mixing stage and before the start of the solid phase polymerization, the solid phase polymerization being conducted in the presence of the nucleator uniformly dispersed in the polymerization mixture. It is preferred that said nucleator is added at any time before the polymerization mixture has reached an intrinsic viscosity of 0.5. The nucleator is preferably a

fine powder of one or more of; boron nitride, a silicate, a metal carbonate, a sulfate, an inorganic metal oxide, a metal salt of an aliphatic (C9 to C30) carboxylic acid, a metal salt of an aromatic carboxylic acid, a metal salt of a polyoxyalkylene carboxylic acid, a metal salt of an olefin-acrylic acid copolymer, an alkali metal chelate compound of acetylacetone; or the nucleator may be an organic nucleator compound.

In other words, the invention is a method of manufacturing highly polymerized polybutylene terephthalate by the solid phase polymerization process in which polybutylene terephthalate obtained from the liquid phase polycondensation of an acid component mainly comprising terephthalic acid or its lower alcohol esters with a diol component mainly comprising 1,4-butanediol is solidified and further subjected to polymerization treatment in a solidified state, characterized in that 0.001% to 5% by weight of a nucleator based on the polycondensate is added thereto for an arbitrary period of time during the liquid phase polycondensation and preferably after the monomer mixing stage, but before the initiation of the solid phase polymerization; and the solid phase polymerization is performed in the homogeneous presence of the nucleator.

The polybutylene terephthalate referred to in this invention, may contain up to 10% per mol of other comonomers. They include, for example, glycol components such as ethylene glycol, propylene glycol, hexamethylene glycol, and bisphenol A, dicarboxylic acids such as isophthalic acid, naphthalenedicarboxylic acid, and adipic acid, and poly-functional compounds such as pentaerythritol, trimethylolpropane, trimellitic acid, pyromellitic acid, hydroxybenzoic acid, and hydroxynaphthoic acid.

The liquid phase polycondensation is conducted according to the conventional method wherein esterification or an ester exchange reaction is followed by polycondensation.

The esterification reaction of terephthalic acid with 1,4-butanediol (hereinafter referred to as "1,4 BG"), is normally performed with the ratio of 1:5 mol of 1,4 BG to 1 mol of terephthalic acid under normal or enhanced pressure, and at a temperature of 200° to 240°C, while continuously removing the water formed. The presence of a catalyst, such as a titanium compound, is often advantageous.

The ester exchange reaction is normally performed with dimethyl terephthalate (hereinafter referred to as "DMT"), and 1,4 BG at a mole ratio of from 1:1 to 1:2 under normal pressure and at a

temperature of 150°C to 220°C, while removing methanol formed. To achieve a practically effective reaction rate, the use of a catalyst is necessary. Examples of the catalyst include titanium compounds, lead oxide, lead acetate, zinc oxide, zinc acetate, and manganese acetate. Especially, preferable are organic titanates and hydrolyzated or alcoholysates of titanium tetrachloride. For example, they include, preferably, organic titanates like tetrabutyl titanate, tetrapropyl titanate, tetraethyl titanae, and tetramethyl titanae, and their hydrolyzates, inorganic titanium compounds like hydrolysates of titanium tetracholoride and titanium sulfate, titanium potassium fluoride, titanium zinc fluoride, titanium cobalt fluoride, etc., and other titanium compounds well known as catalysts for polyester manufacture such as titanium oxalate, and titanium potassium oxalate.

Especially preferable are hydrolyzates of tetrabutyl titanate, tetrapropyl titanate and tiatanium tetrachlorde. .

The amount, in terms of titanium, of such a catalyst used should be 10 to 1,000 ppm of polymer, preferably, 30 to 300 ppm. The addition of the catalyst may be made in several portions during the reaction, as required.

In the polycondensation reaction, the product obatined by the aforementioned esterification or ester exchange reaction is subjected to melt polycondensation at 200° to 260°C under reduced pressure in the reaction system, while continuously removing 1,4 BG and by-products, until the desired polymerization is achieved, thereby yielding the prepolymer. In order to achieve a practically useful reaction rate in the polycondensation reaction, the use of a catalyst is necessary.

The catalysts which can be used herein include those used in the aforementioned esterification or ester exchange reaction and it is practicable further to add one or more of them before initiating the polycondenation reaction for improvement of the rate of the polycondensaiton reaction.

The polycondensate (prepolymer) obtained by the liquid phase polymerization (melt polymerization) is taken out of the reactor, solidified, and ground or granulated prior to being subjected to the solid phase polymerization.

The characteristic feature of this invention lies in the addition of 0.001% to 5% by weight of a nucleator at an arbitrary time after the monomer preparation stage but before the solid phase polymerization. The nucleator addition may be at any time before the initiation of the solid phase

polymerization, but it is preferable that the nucleator is finely powdered and essential that it is homogeneously dispersed, when the solid phase polymerization is performed; to ensure this, it should be added during the first half of the liquid phase polymerization period or before the polycondensation, when the viscosity of the reaction system begins to rise, that is, during the period from the monomer mixing stage to the completition of the esterification or ester exchange reaction, so that it is already added to the reaction system at the time of polycondensation, desirably, to be homogeneously dispersed, taking advantage of the shearing force generated as the viscosity rises. It is also feasible to add the nucleator after the melt polymerization and before entering the solid phase polymerization and to homogeneously disperse it by kneading in an extruder, but this method is undesirable because of the interposition of the extrusion and kneading processes.

Well-known nucleators normally employed for improving the moldability of polyester are used in this invention. They include, for example, boron nitride, talc, kaolin, bentonite, clay, graphite, asbestos, silica, silicates such as calcium silicate, metal carbonates such as calcium carbonate and magnesium carbonate, sulfates such as

calcium sulfate and barium sulfate, inorganic oxides such as titanium oxide, calcium oxide, aluminium oxide, molybdenum oxide and silicon oxide, metal salts of higher aliphatic mono- or di-carboxylic acids having 9 to 30 carbon atoms, such as lauric acid, myristic acid, palmitic acid, oleic acid, stearic acid and montanic acid, metal salts of aromatic mono- and di-carboxylic acids such as benzoic acid and phthalic acid, or aromatic alkyl mono- and di-carboxylic acids or their derivatives, metal salts of carboxylic acids having polyoxyalkylene groups, metal salts of olefin-acrylic acid copolymers, alkali metal chelates of acetylacetone, and aromatic organic compounds such as benzophenone, oxybenzoate and polyarylene esters. These compounds may be used singly or in a combination of two or more.

The metals of the aforementioned metal salt compounds should preferably be, but not restricted to, alkali or alkaline earth metals such as sodium, lithium, calcium, magnesium or barium.

Of the aforementioned nucleators, the one especially desirable for the method of this invention is boron nitride.

The aforementioned nucleators, if in the form of solid particles, are the more effective, the smaller the final particle diameter; they should be smaller than at least 100 microns, preferably

smaller than several microns or further preferably smaller than 1 micron. According to this aspect of the preferred method provided by this invention, the shearing force generated during the polycondensation reaction due to the high viscosity of the reaction system, is effective in dispersing the particles of such diameter finely and homogeneously, and it will be apparent that the nucleator should, desirably, be pulverised into fine particles, before being added to the reaction system.

The amount of the nucleator used according to this invention, should be in the range of 0.001% to 5% by weight, depending on the type; in particular, the amount used is preferably 0.005% to 3% by weight.

Well-known stabilizers, such as sterically hindered phenol or phosphorus compounds, etc., may be added during the monomer mixing stage or the liquid phase polycondensation.

The polybutylene terphthalate prepolymer, which has been melt-polymerized in the presence of the nucleator, has intrinsic viscosities in the order of 0.5 to 1.2; it is then solidified by cooling and subjected to the solid phase polymerization after being crushed or granulated. The solidificaiton by cooling is conducted by ordinary methods. For example, the prepolymer

delivered from the melting reactor in the shape of sheet or strand is solidified by cooling, by being passed through an air current, or through water, and then crushed or cut. It is advantageous to produce granules having as uniform a size as possible, so that an increase in the molecular weight should be made uniformly during the solid phase condensation. Desirably, particle diameters should be 1 to 5mm. According to the method of this invention, immediately thereafter, the granules may be transferred to a solid phase polymerization reactor, which is adjusted to an appropriate temperature, to effect the solid phase polymerization.

In the conventional solid phase polymerization method wherein no nucleator is used, pretreatments such as drying or crystallization, by holding the prepolymer at an appropriate temperature (120°to 180°C) for a long time (3 to 6 hours) are required before the solid phase polymeriztion should be conducted. Otherwise, polymer particles will mutually fuse together, forming agglomerates during the solid phase polymerization or the polymerization in the solid phase will barely proceed or will be very slow, taking a long time to complete. In contrast, when the nucleator is added and homogeneously dispersed at the time of melt polymerization, as in the method of this invention,

no fusion of polymer particles occurs, and a sufficiently highly polymerized polymer can be obtained at high efficiency, even when such pretreatments are ommitted, so that the productivity can be improved through simplification of the process, curtailment of the time, etc.; and the economic advantage achieved is remarkable. Even in the method of this invention, drying or storing, if required for production, are not prohibited.

The solid phase polymerization of the method of this invention can be performed by commonly known methods except for dispensing with pretreatments such as preliminary crystallization.

Thus, after the melt polymerization, the solidified and ground intermediate condensate (as the case may be, after removing excess liquid cooling medium present on the surface of the formed particles) with an intrinsic viscosity of 0.5 to 1.2, is directly put in a reactor held at a temperature lower than its melting point by 5° to 60°C. This reactor, being provided with adequate gas inlet, exhaust port and an appropriate vacuum coupler, is suitable for solid phase condensation. For example, the solid phase condensation may be performed in this reactor in an inert gas current or in vacuum. The reactor used in this manufacturing method, is well known per se, and is

not critical in this invention, and therefore its detailed description is omitted; either batch type or continuous type are feasable; anyway, it is only proper that such a reactor permits the intermediate condensate to stay therein until the intended intrinsic viscosity is obtained and is capable of maintaing a uniform reaction temperature; the desired viscosity may be appropriately controlled throught by the adjustment of residence time and treating temperature.

Effects of the Invention

The effects of this invention, as is clear from what has already been described, are such that, with the nucleator added during the liquid phase polymerization, particularly, at the time of mixing raw materials, or at a stage before the reactants attain high viscosities through polycondensation, it is treated for a long time under the shearing force of the high viscosity molten polymer before the polycondenation is accomplished; therefore, it affords very fine particles which are homogeneously dispersed, so that the nucleating action may be bolstered and a high degree of crystallinity can be achieved, without necessitating such pretreatments as crystallization, after cooling and grinding; accordingly, even when the transition to the solid

phase polymerization is immediate, no fusion of the polymer particles will occur, permitting highly polymerized polymer to be produced at high efficiency and in a short time; as a result, the simplification of the process and the curtailment of the time involved, will bring about a large economic advantage.

It is well known that the addition of the nucleator promotes crystallization, aids in the mold releasing operation, improves the molding cycle and ameliorates the physical properites of the molded articles and, the solid phase polymer obtained by the method of this invention is also provided with a well known moldability effect and this effect is enhanced through the homogeneous dispersion, rather than by the conventional method of addition; but it has still other charateristic effects which reside in the discovery that the nucleator effect can be very effectively utilized, aside from the moldability, for improvement in economy through an increase in the polymerization rate and rationalization of the process as described above in the solid phase polymerization and the method of manufacturing high molecular weight polybutylene terephthalate based on this discovery. Such a solid phase polymerization process has not previously been known at all.

Examples

In the following, examples of this invention will be described, though this invention is by no means bound thereby.

TABLE 1

Examples 1 to 16 and Comparative Example 1

Into a reactor having a stirrer, nitrogen inlet and a separating column, 100 parts by weight of dimethyl terephthalate, 95 parts by weight of 1,4-butanediol and 0.06 part by weight of titanium tetraisopropylate was fed, with various types of nucleators in quantities as shown in Table 1 added in a state of suspension and dispersion, using part of the aforementioned 1,4-butanediol. About 90% of the theoretical amount of methanol formed within 15 hours was distilled off, while stirring under nitrogen. The temperature of the reaction mixture rose to 200°C. Then the mixture was transferred to a second reactor, which was evacuated to 0.5 mm Hg within 1.0 hour and simultaneously therewith, the reaction temperature was raised to 255°C. Two hours later, the reaction was completed; then, the molten product was extruded from an ejector port as a strand; this strand was cooled with water; the adherent water was removed by passing it through hot air and the product was cut into a colourless cylindrical granule of a size 2x3mm. The intrinsic

viscosity of this prepolymer was of the order of 0.75 to 0.80. The granular prepolymer was put in a rotary flask immersed in an oil bath held at 200°C and the granules were stirred and mixed, while turning the flask and keeping a vacuum of 0.3 mm Hg, thereby carrying out the solid phase polymerization for about 6 hours.

The intrinsic viscosities of the solid phase polymerized polymers thus obtained are depicted in Table 1. (Examples 1 to 16).

For comparison, values obtained without addition of the nucleator are also listed in Table 1. (Comparative example 1).

Table 1

	Type of nucleator	Amount of addn. (% by wt. of polymer)	Intrinsic viscosity after solid phase polymerization
Comp. Ex 1	—	0	0.95
Example 1	boron nitride	0.005	1.18
" 2	"	0.010	1.48
" 3	"	0.10	1.58
" 4	talc	0.10	1.02
" 5	"	0.5	1.18
" 6	"	1.0	1.30
" 7	fine powder silica	0..10	1.10
" 8	"	0.100	1.38
" 9	calcium carbonate	2.0	1.12
"10 10	barium sulfate	2.0	1.15
" 11	sodium laurate	1.0	1.23
" 12	barium laurate	1.0	1.21
" 13	calcium stearate	1.0	1.03
" 14	calcium montanate	1.0	1.15
" 15	sodium benzoate	1.0	1.22
" 16	metal salts of ethylene methacrylic acid copolymer	1.0	1.31

TABLE 2

Examples 17 to 24 and Comparative Example 1

The melt polycondensation was performed under exactly the same conditions as in the aforementioned examples, except that the addition of the nucleator in the liquid phase polymerization was made at the time of transfer from the aforementioned first reactor to the second reactor (that is, after the ester exchange reaction and before the polycondenation reaction). In this instance, the intrinsic viscosity of the prepolymer was 0.75 to 0.80. Thereafter, it was subjected to the solid phase polymerization exactly in the same manner as described above.

The intrinsic viscosities of the polymers after the solid phase polymerization are given in Table 2.

Table 2

	Type of nucleator	Amount of addn. (% by wt. of polymer	Intrinsic viscosity after solid phase polymerization
Comp. Ex 1	—	0	0.96
Example 17	boron nitride	0.005	1.16
Example 18	"	0.010	1.50
Example 19	talc	1.0	1.28
Example 20	fine powder silica	1.100	1.35
Example 21	calcium carbonate	2.0	1.10
Example 22	sodium laurate	1.0	1.25
Example 23	calcium montanate	1.0	1.18
	metal salts of ethylene methacrylic acid copolymer	1.0	1.30

TABLE 3

Examples 25 and 26 and Comparative Example 2

The granular prepolymer (intrinsic viscosity: 0.76) obtained by melt polymerization under exactly the same conditons as in Examples 3 and 6 was fed to the top of a longitudinally cylindrical solid phase reactor with a jacket (through which 220°C heating medium passed) through a preheater (staying for 30 min), heated to a specified level in the reactor so as to hold it for a specified residence time, and drawn out from the bottom, while nitrogen, dried and held at 270°C, was fed in from the bottom and discharged from the top, whereby continuous solid phase polymerization was carried out in a nitrogen current. The internal temperature of the reaction system was 210°C at its top, 213°C at its middle part, and 215°C at its bottom, while the residence time was about 8 hours. The intrinsic viscosities of the solid phase polymerized polymer thus obtained are shown in Table 3. Values obtained by exactly the same operation without addition of nucleators are also listed in this table for comparison.(Comparative example 2).

Table 3

	Type of nucleator	Amount of addn. (& by wt. of polymer)	Intrinsic viscosity after solid phase polymerization
Comp. Ex. 2	——	0	0.98
Example 25	boron nitride	0.01	1.51
Example 26	talc	1.0	1.32

CLAIMS

1. A process for manufacturing a polybutylene terephthalate, which comprises the steps of polycondensating, in the liquid phase, terephthalic acid, or a lower alcohol ester thereof as the acid component, and 1,4-butanediol as the diol component, to obtain a prepolymer of polybutylene terephthalate;

solidifying the prepolymer,

and further polymerizing the prepolymer in the solid phase to obtain a polybutyrene terephthalate of a higher polymerization degree;

0.001 to 5 percent by weight, based on the prepolymer, of a nucleator being added to the polymerization mixture at any time during or following the monomer-mixing stage and before the starting of the solid phase polymerization:

the solid phase polymerization being conducted in the presence of the nucleator uniformly dispersed in the polymerization mixture.

2. A process as claimed in Claim 1, in which said nucleator is added at any time until an intrinsic viscosity of the polymerization mixture has reached 0.5.

3. A process as claimed in Claim 1, in which said nucleator is a fine powder of one or more of boron nitride, a silicate, a metal carbonate, a sulfate, an inorganic metal oxide, a metal salt of an aliphatic (C9 to C30) carboxylic acid, a metal salt of an aromatic carboxylic acid, a metal salt of a polyoxyalkylene carboxylic acid, a metal salt of an olefin-acrylic acid copolymer, and alkali metal chelate compound of acetylacetone.

4. A process as claimed in Claim 1, in which said nucleator is an organic nucleator compound.

5. A process as claimed in Claim 1, in which said nucleator has a particle size of 100 microns or smaller.

6. A process as claimed in Claim 1, in which the solid phase polymerization is carried out after the prepolymer cooled and solidified has been crushed into granules.